THE WATER SOLUBILITY OF SOME LOW MOLECULAR WEIGHT MERCAPTANS

by

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ABSTRACT

Certain mercaptans play an important role as modifiers and promoters in the butadiene-styrene copolymerization reaction in the manufacture of synthetic rubber. The water solubility of mercaptans is one of the factors believed to influence the effectiveness of the mercaptan as a promoter.

In this research, attempts have been made to purify some low molecular weight mercaptans and to measure their water solubility. The purification method involved the precipitation of the lead mercaptide followed by recrystallization of this salt and recovery of the mercaptan by decomposing with dilute sulfuric acid. The lead mercaptide was formed by mixing alcoholic solutions of mercaptan and lead acetate. Ethanol, ethanol-pyridine and ethanol-benzene were used as recrystallization solvents. The melting points obtained for these lead salts were: ethyl mercaptide 124°, n - propyl mercaptide 94°, isopropyl mercaptide 85-87°, n - butyl mercaptide 80°, isobutyl mercaptide 97-99°, n - pentyl mercaptide 82.5°, n - hexyl mercaptide 89° and n - heptyl mercaptide 88°. An amperometric titration method was used to measure the water solubility of mercaptans at 25°. The results in moles per litre are as follows: ethyl 1.52×10^{-1}, n - propyl 3.50×10^{-2}, isopropyl 4.77×10^{-2}, n - butyl 8.24×10^{-3}, isobutyl 10.02×10^{-3}, n - pentyl 2.22×10^{-3}, n - hexyl 5.00×10^{-4} and n - heptyl 1.75×10^{-4}.

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THE WATER SOLUBILITY OF SOME LOW MOLECULAR WEIGHT MERCAPTANS

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INTRODUCTION

Mercaptans or thioalcohols are a group of organic chemicals whose chief characteristic is the sulfhydryl group. The aliphatic members of this group have gained importance in the synthetic rubber industry in recent years. They are used extensively as promoters and modifiers for the persulfate catalyzed copolymerization of butadiene and styrene to form synthetic rubber. In the presence of mercaptan the rate of reaction is nearly independent of both the mercaptan and persulfate concentration within wide limits. (4) The action of the mercaptans as promoters is that of a chain transfer agent. The mechanism of transfer of chain activity by the mercaptan may be symbolized as follows:

$$R^{\bullet}m + RSH \longrightarrow RmH + RS^{\bullet}$$

$$RS^{\bullet} + M \longrightarrow RSM^{\bullet}$$

$R^{\bullet}m$ represents the activated growing polymer molecule, RSH represents a molecule of mercaptan, and $RS^{\bullet}$ represents the free radicle from the mercaptan which starts the growth of a new polymer molecule, and M represents a monomer molecule. (5) In addition the amount ofmercaptan affects the properties of the rubber. With very small amounts, the polymer is hard, tough and not very soluble in benzene. Polymers prepared with somewhat larger amounts of mercaptans are softer, more soluble in benzene, and in general have properties which allow for easier processing of the polymer. With too large amounts of mercaptan the polymer becomes almost sticky. (5)

Until recently most of the production of synthetic rubber by polymerization has been carried out at 50° using n-dodecyl mercaptan. In recent years polymerization recipes have been developed which allow the reactions to be carried out at lower temperatures using low molecular weight mercaptans as promoters and modifiers. The polymerization is carried out in a soap-water emulsion, and prior to entering the reaction, the mercaptan must move from an organic phase, across a water boundary to the locus of reaction in a soap micelle. The diffusion coefficient and the water solubility of mercaptans are two of the factors believed to govern the rate of migration across this barrier.

Little work has been done on the determination of the properties of mercaptans and their salts. Yabroff (13) determined the water solubilities of some of the low molecular weight mercaptans by means of a potentiometric titration with silver nitrate. His results are shown in Table I.

TABLE I

Solubility of Mercaptans in Water at 20°C as Determined by Yabroff. (13)

Mercaptan	Solubility (Moles/litre)
ethyl	1.12×10^{-1}
n - propyl	2.50×10^{-2}
n - butyl	6.61×10^{-3}
t - butyl	1.07×10^{-2}
n - amyl	1.53×10^{-3}
n - heptyl	7×10^{-5}

Yabroff appears to have taken no precautions to prevent volatilization or oxidation of the mercaptans before the titration and Maerov (10) has shown that neglecting these precautions will give low results. The results of Maerov are shown in Table 2.

TABLE 2

Solubility of Mercaptans in Water at 25°

as Determined by Maerov (10)

Mercaptan	Solubility (Moles/litre)	% Purity of Mercaptan
ethyl	1.32×10^{-1}	95.2
n - propyl	3.07×10^{-2}	96.1
iso - propyl	4.46×10^{-2}	91.7
n - butyl	7.40×10^{-3}	99.2
sec - butyl	8.80×10^{-3}	96.5
t - butyl	1.50×10^{-2}	91.4
sec - amyl	2.76×10^{-3}	96.7
t - amyl	4.05×10^{-3}	99.7
n - hexyl	6.70×10^{-4}	90.9
t - hexyl	1.20×10^{-3}	92.5
t - heptyl	3.70×10^{-4}	82.5
n - octyl	1.03×10^{-4}	94.5
t - octyl	3.78×10^{-4}	80.4

Maerov pipetted a definite volume of mercaptan solution, added it to ethanol and titrated to an amperometric end point with silver nitrate. Goward (2) determined the water solubility of some high molecular weight mercaptans.

He used a radioactive tracer method and an amperometric titration method. Using partially purified n - decyl mercaptan, he found that impurities in the mercaptan impose an indefinite error on the accuracy of the measurement of solubility. Impurities such as hydrogen sulfide and low molecular weight mercaptans increase the apparent solubility. Impurities other than those mentioned above, such as the corresponding disulfide in the mercaptan phase, would appear to cause a decrease in the apparent solubility. Consideration of the chemical potentials of the mercaptan in the mercaptan phase and in the water phase show that impurities such as the disulfide would lower the apparent solubility of the mercaptan. More simply, the system may be considered as having three phases, and the mercaptan, being more soluble in the impurity phase than the water phase is extracted from the water phase.

Formation of a disulfide suspension in the water phase, however, would extract mercaptan from the water phase. The water is held at saturation concentration by contact with excess mercaptan. Since the concentration of mercaptan in the disulfide phase is greater than that in the water, the average concentration of mercaptan in the system will be greater than it would be in the absence of the disulfide suspension.

Purification of a mercaptan salt followed by decomposition of the mercaptide should result in removal of most of the impurities. Preparation of pure lead mercaptide was attempted by Borgstrom et al (6). The lead mercaptide

was prepared by mixing alcoholic solutions of mercaptan and lead acetate until a cloudiness appeared. It was then heated to boiling, more alcohol added if necessary to clear the solution, and allowed to cool to crystallize the lead salt. He found that on recrystallization the product was more unstable and did not have a constant melting point. Wertheim (12) prepared lead mercaptides as possible derivatives for identification of mercaptans. He precipitated the mercaptides from ethanolic solutions of lead acetate and recrystallized once from an appropriate solvent. His results are shown in Table 3. The lead salts whose melting points are not reported precipitated as gummy masses which did not harden for some time. The solvent used in these cases was not mentioned.

TABLE 3

Melting Points of Lead Salts of Mercaptans as Determined by Wertheim (12)

Mercaptan	Melting Points of Lead Salts °C	Solvent Used for Recrystallization
methyl	gummy mass	--
ethyl	* 150°	--
propyl	gummy mass	--
iso propyl	91 - 92	EtOH
butyl	80 - 81	$CHCl_3$ + EtOH
iso butyl	gummy mass	--
amyl	gummy mass	--
iso amyl	gummy mass	--
heptyl	94 - 95	benzene

* value reported in Mulliken (8)

A gravimetric determination of molecular weight and mercaptan content of mixtures of primary mercaptans was devised by Laitinen et al (9), which involved the amperometric titration of absolute alcohol solutions of mercaptans with silver nitrate. The average molecular weight and percent mercaptan was calculated from the titration results and from the weight of the silver mercaptide precipitate.

The work embodied in this thesis involves the purification and subsequent measurement of the water solubility of some low molecular weight aliphatic mercaptans.

EXPERIMENTAL

A. Materials

The mercaptans used were obtained from Eastman Kodak Company. These were of reagent grade except for ethyl mercaptan which was of technical grade and isopropyl mercaptan which was of practical grade. Some of the pyridine used for recrystallization was of reagent grade. The technical grade pyridine was purified by distillation from zinc dust. The pyridine was reclaimed for re-use by distillation. Reagent silver nitrate was used directly as a primary standard. Ninety-five percent ethyl alcohol was used in the experimental work. All other chemicals used were reagent grade. The water used was ordinary distilled water.

B. Apparatus

The principal problems encountered in obtaining reliable measurements of water solubility of mercaptans are: (1) oxidation of the mercaptan, (2) loss of mercaptan due to volatilization and (3) formation of a water - mercaptan emulsion. The apparatus was designed to minimize these effects. Air oxidation of mercaptan will produce the disulfide according to the following equation:

$$4RSH + O_2 \rightarrow 2R\text{-}S\text{-}SR + 2H_2O$$

where R represents an alkyl radical

The low molecular weight mercaptans have high vapor pressures and tend to distill from solution. Emulsification, which would cause an increase in the apparent solubility of the mercaptan, could be caused by too vigorous stirring. Rapid stirring

would draw droplets of mercaptan into the solution and these droplets, when hit by the stirrer, could break into colloidal size particles which would remain in suspension and increase the apparent solubility of the mercaptan.

A schematic diagram of the apparatus is shown in Figure 1. Nitrogen scrubbed in a chromous chloride tower (A) could enter the solubility flask (B) either above the liquid, or it could be bubbled through the water. Since the mercaptan seemed to be absorbed by rubber stoppers, the solubility flask was fitted with a paraffin wax coated cork (C). The magnetic stirrer (D), used to keep the water phase homogeneous, turned at the rate of one or two revolutions per second. Because a magnetic stirrer as ordinarily set up revolved at a greater speed, the rotation rate was decreased by attaching the primary magnet to a Mixmaster motor by a reducing pulley arrangement. The amperometric titration unit (E) consisted of a saturated calomel half cell (F) as a source of potential, connected through a microammeter (G) to a rotating platinum microelectrode (H). Chloride was eliminated by using a three percent agar - thirty percent potassium nitrate salt bridge (I) between the calomel cell and the solution titrated.

C. Method

The experimental work is described in three parts; purification of the mercaptans, estimates of their purity, and their water solubility. All temperatures are reported in Centigrade degrees.

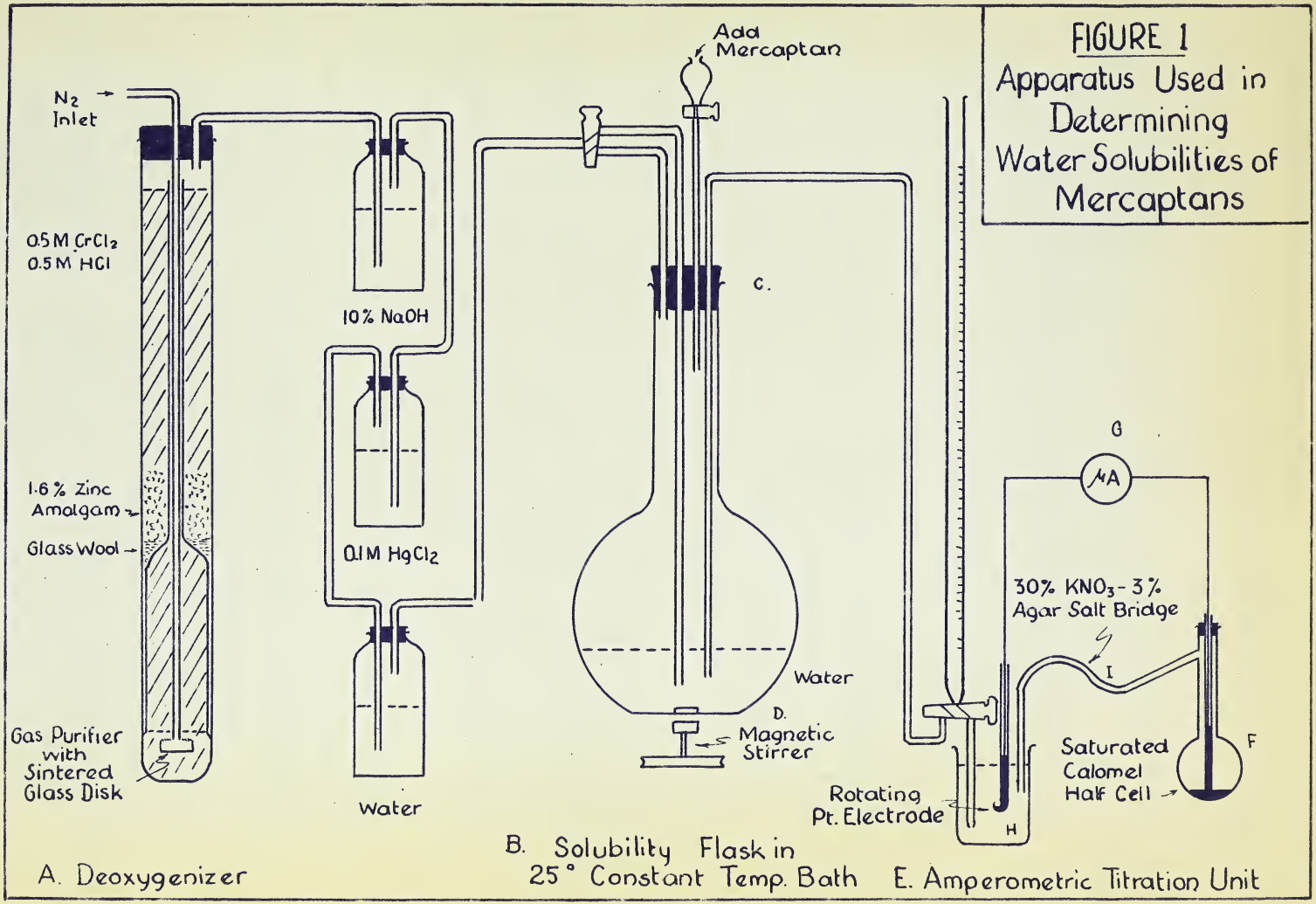

FIGURE 1
Apparatus Used in Determining Water Solubilities of Mercaptans

1. Purification of the Mercaptans

Since impurities in the mercaptan will not allow reliable measurements to be made, they must be purified before measurements are made using them. They have been purified for this study in the following way.

The mercaptan was precipitated from ethanol as the lead mercaptide. A 1:1 ethanol to mercaptan solution was added slowly to a warm 20-25 percent solution of lead acetate in ethanol. The mixture was cooled to 0° or colder and allowed to crystallize for several hours. After suction filtration and drying, excess lead acetate was extracted from the crude product with water. The lead mercaptide was recrystallized from an appropriate solvent and air dried at room temperature.

The mercaptans from ethyl to hexyl were recovered from the pure lead salt by decomposition with dilute sulfuric acid, and distillation of the mercaptan. The receiver for the mercaptans with low boiling points was immersed in a salt-ice bath to reduce volatilization losses. The distillate was washed with distilled water, a 10 percent sodium carbonate solution and again with distilled water. The mercaptan was then dried over anhydrous sodium sulfate and redistilled. Because of its high boiling point (169°) n - heptyl mecaptan, was separated from the sulfuric acid - lead sulfate mixture using a separatory funnel, washed with sodium carbonate solution, distilled water and then distilled. This distillate was then washed, dried and redistilled.

The lead content of the lead mercaptides was determined by weighing approximately 0.5 g samples of lead mercaptide and decomposing them with 30 ml of dilute nitric acid. This solution was evaporated just to dryness and the residue analysed for lead using an iodometric titration (7).

2. Estimation of Purity of the Mercaptan

Two estimates of purity of the mercaptans were obtained. The boiling points of the purified mercaptans were constant for the entire volume collected. This generally indicates a pure liquid rather than a mixture. For the second estimate a modification of the gravimetric method of Laitinen et al (9) was used to determine the average molecular weight of the mercaptan. A sample of the mercaptan was weighed in a Victor Meyer weighing bottle and added to an alcoholic solution of silver nitrate containing either the theoretically equivalent amount of silver nitrate or slightly less. The silver mercaptide was filtered through Gooch crucibles and dried to constant weight at 110° in an ordinary oven. The molecular weight was calculated from the weight of precipitate and the volume of silver nitrate using the following equation:

$$\text{molecular weight} = \frac{1000W}{A \times N} - 106.9$$

W = wt. of silver mercaptide

A = ml. of silver nitrate

N = normality of silver nitrate

106.9 = atomic weight of silver - atomic weight of hydrogen.

Sample Calculation

Following is an example of the molecular weight calculation.

The reaction during precipitation is:

$$Ag^+ + RSH \rightarrow AgSR + H^+$$

where RSH represents mercaptan.

Mercaptan -- iso butyl, molecular weight 90.19

Normality of $AgNO_3$ -- 0.1200

Weight of mercaptan -- 0.1044g

Theoretically equivalent amount of silver nitrate required: $\frac{0.1044}{90.19} \times \frac{1000}{0.1200} = 9.65$ ml.

Weight of precipitate of silver mercaptide obtained = 0.2272g

Molecular weight = $\frac{1000 \times 0.2272}{9.65 \times 0.1200} - 106.9 = 89.5$

The deviation is about seven parts in 900. This is within the expected limits of experimental error.

3. Measurement of the Water Solubility of Mercaptans

A modification of the amperometric titration method of Kolthoff and Harris (6) was used to measure the concentration of mercaptan in the water solutions. Since chloride is excluded from the system a neutral rather than ammoniacal indifferent electrolyte could be used during the titration. In this case silver in the form of the silver ion, is electroreducible at the potential of a saturated calomel half cell.

Nitrogen, purified in a chromous chloride deoxygenizer, was bubbled through the water to displace any dissolved oxygen and was used as an inert atmosphere during

the solubility measurements. Exess mercaptan was added through a dropping funnel into a 2 litre flask containing oxygen free distilled water. Nitrogen pressure was used to force a sample of the solution into the attached burette. (see Figure 1)

An accurately measured 10 ml volume of aqueous silver nitrate of appropriate and known concentration in 160 to 200 ml ethyl alcohol was titrated to an amperometric end point with the mercaptan solution. Five to ten grams of ammonium acetate were used as an indifferent electrolyte. Asbestos fibre was added to the silver nitrate solution to prevent silver mercaptide from coating the rotating platinum electrode and decreasing its effective surface area. The tip of the burette containing the mercaptan solution was below the surface of the alcoholic silver nitrate solution. In this way loss due to volatilization was minimized because the mercaptan is soluble in alcohol and reacts rapidly with the silver ion. Rather than pure ethanol a 50 percent ethanol solution of 0.001 N silver nitrate was used during the titration of n - hexyl and n - heptyl mercaptans. This was necessary because with a pure ethanol solution, the current, with this dilute silver nitrate solution, was of the order of two to four microamperes. This current is too small to give accurate results. With some water present the current was increased to about 12 microamperes. On the other hand, when the alcohol was completely replaced by water the relationship between volume of mercaptan solution added and current was not linear.

Plotting current in microamperes vs volume of mercaptan solution resulted in a straight line at low silver ion concentration. The points were extrapolated to 0 microamperes to find the equivalence point. The reaction during the titration may be represented by:

$$RSH + Ag^{+} \rightarrow H^{+} + RSAg$$

One mole of mercaptan is equivalent to one mole of silver nitrate in this reaction and the calculation of the concentration of the mercaptan in solution is simply:

$$ml_{AgNO_3} \times M_{AgNO_3} = ml_{RSH} \times M_{RSH}$$

Where ml_{AgNO_3} = volume of silver nitrate in solution titrated.

M_{AgNO_3} = molarity of silver nitrate

ml_{RSH} = equivalent volume of mercaptan solution

M_{RSH} = molar concentration of mercaptan in mercaptan solution.

The mercaptan solution was analyzed for mercaptan content at regular intervals, and from data obtained a time-concentration curve was plotted for each mercaptan. Initially, concentration increased rapidly with time, but reached a limiting value after 7 to 14 hours. The concentration corresponding to the plateau of the resulting Langmuir type curve was assumed to be the saturation concentration.

D. Results and Discussion.

1. Characteristics of Lead Mercaptides

Lead salts of the mercaptans were prepared by mixing alcoholic solutions of mercaptan and lead acetate. These mercaptides were purified by recrystallization from an

appropriate solvent. The most suitable solvents for the low molecular weight mercaptides were ethanol, ethanol-pyridine mixture, and ethanol-benzene mixture. The isopropyl mercaptide was recrystallized from ethanol. All the other mercaptides prepared were insoluble in ethanol. A mixture of ethanol and pyridine was found to be the most suitable solvent for the lead salts of ethyl to butyl mercaptans inclusive. Benzene and benzene - ethanol mixtures either caused decomposition, that is, the solution became black, or else the mercaptide would not recrystallize. For n - pentyl to n - heptyl mercaptides inclusive, a benzene - ethanol mixture was used as recrystallization solvent. The ethanol - pyridine solution would not dissolve appreciable amounts of these mercaptides. The purified lead salts had the characteristics shown in Table 4.

TABLE 4

Characteristics of the Purified Lead Mercaptides

Mercaptan	Melting point of Mercaptide		Recrystallization Solvent	% Lead Theor.	% Lead Found.
ethyl	124°		ethanol + pyridine	62.87	62.69
n - propyl	94		ethanol + pyridine	57.95	57.44
isopropyl	85 - 87		ethanol	57.95	59.31
n - butyl	80		ethanol + pyridine	53.72	53.53
isobutyl	97 - 99		ethanol + pyridine	53.72	53.93
n - pentyl	82.5	3:7	ethanol - benzene	50.01	51.53
n - hexyl	89	7:3	ethanol - benzene	46.91	46.94
n - heptyl	88	7:3	ethanol - benzene	44.11	44.66

In most cases the melting points were slightly lower than those reported by Wertheim (12) (see Table 3). However, the lead salts had sharp melting points, except for the isopropyl and isobutyl mercaptides, which melted over a range of 2 degrees. The melting point of lead ethyl mercaptide was 124° compared to 150° reported in Mulliken (11). No other value for the melting point of this compound was found in the literature reviewed. The mercaptides crystallized as bright yellow needles, which decreased in length from about one half centimeter for ethyl mercaptide to very fine needles for n - heptyl mercaptide. n - Propyl mercaptide is an exception in that it crystallized as shining yellow plates. All the mercaptides formed "oils" when heated with insufficient solvent but only the isobutyl mercaptide formed an oil after filtration of the hot solution. However, in all cases, the oil solidified rather than forming a gummy mass.

The dry recrystallized mercaptides appeared to be stable in air. The crude products seemed more unstable, that is, they smelled very strongly of mercaptan and had a tendency to change from a bright yellow color to white. Ethyl mercaptide dried in a vacuum dessicator over phosphorous pentoxide darkened a little and appeared to decompose. The melting point was lower and not as sharp as for the air dried material.

Extraction of excess lead acetate was necessary because it would recrystallize in much the same manner as

the lead mercaptide.

Initial work with lead ethyl mercaptide showed that the crude product had a higher melting point than the recrystallized salt (128° compared to 124°), in addition, the literature value for the melting point of this salt was 150° compared to 124° found. The melting points of some mixtures of lead acetate and lead mercaptides were determined to see whether a lead acetate impurity would raise the melting point. Three samples were mechanically mixed using a mortar and pestle and three were crystallized together from a pyridine - ethanol solution. In the latter case mercaptan content was determined indirectly by decomposing the lead mercaptide with dilute sulfuric acid and distilling the mercaptan into a 50 percent ethanol solution containing excess standard silver nitrate. Excess silver was titrated by the Volhard method (8). The results indicate a minimum type phase diagram which is common for mixtures. Figure 2.

The graph indicates that lead acetate impurity would lower rather than raise the melting point of the lead ethyl mercaptide. Since the purified lead mercaptide was air dried at room temperature, possibly a small amount of the recrystallization solvent remained in contact with the salt and lowered its melting point. Ethyl alcohol, from which the mercaptide was originally precipitated should evaporate more completely, as it does not seem to wet the dry mercaptide. Two factors which indicate only a small amount of impurity, if that is the cause of the lower melting point,

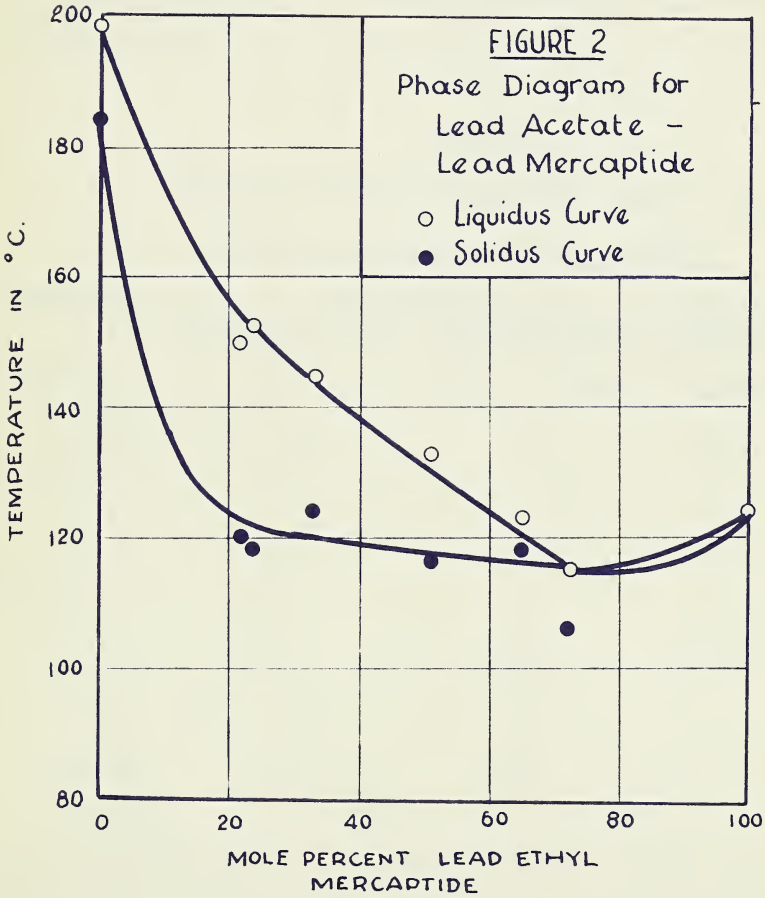
FIGURE 2
Phase Diagram for
Lead Acetate -
Lead Mercaptide
○ Liquidus Curve
● Solidus Curve
200
180
160
140
120
100
80
TEMPERATURE IN °C.
0
20
40
60
80
100
MOLE PERCENT LEAD ETHYL
MERCAPTIDE

are the lead analysis and the sharp melting point of the lead mercaptide.

2. Effectiveness of Purification of Mercaptan

The effectiveness of the purification procedure was estimated by determining the molecular weight and the boiling point of the mercaptan. Table 5 compares the theoretical molecular weight to the molecular weight found, and Handbook values (3) for boiling points to the uncorrected boiling points which were determined.

TABLE 5

Boiling Points and Average Molecular Weights of Purified Mercaptans

Mercaptan	Boiling Point °C		Molecular Weight	
	Handbook Value	Experimental	Theor.	Found
ethyl	34.7	32.5 - 33.5	62.13	62.1
n - propyl	67 - 68	66	76.16	74.5
isopropyl	60	49 - 50	76.16	75.5
n - butyl	98	94.5	90.19	90.1
isobutyl	88	86	90.19	88.3
n - pentyl	126	120	104.21	101.8
n - hexyl	149 - 50	145	118.24	115.7
n - heptyl	176.2	169	132.27	132.1

The results of the molecular weight determinations are not necessarily indicative of the purity of the mercaptan because of the modifications of procedure, recommended by Laitinen (9), which were used. Rather than titrating an alcohol solution of the mercaptan to an

amperometric end point with silver nitrate, the mercaptan was added directly to an alcoholic silver nitrate solution. The precipitation of the mercaptide was carried out in this way to reduce volatilization losses. Gooch crucibles were used in preference to sintered glass crucibles because coarse sintered glass did not retain all of the precipitate. The precipitates were dried in an ordinary oven at 110° rather than at 60 - 70° in a vacuum oven. Some decomposition probably occurred at the higher drying temperature, which would produce low values in the molecular weight determination.

No stem correction or pressure corrections were applied to the boiling points reported in Table 5. The boiling points are comparable to values reported in the Handbook of Chemistry and Physics (3) except for isopropyl mercaptan. The boiling point found was 49 - 50° compared to 60° in the Handbook and 57 - 60° in Mulliken (11).

3. Water Solubility of Mercaptans

The water solubility of some low molecular weight mercaptans, that is, those containing from two to seven carbon atoms was determined. Saturation concentration for each mercaptan was assumed to be the value corresponding to the plateau of the Langmuir type curve obtained by plotting mercaptan concentration vs time in hours. The graph for each mercaptan is reproduced in Figures 3 to 10. The mercaptans containing from two to five carbon atoms follow a Langmuir type curve. The time vs concentration curves for n - hexyl and n - heptyl mercaptans were not as expected.

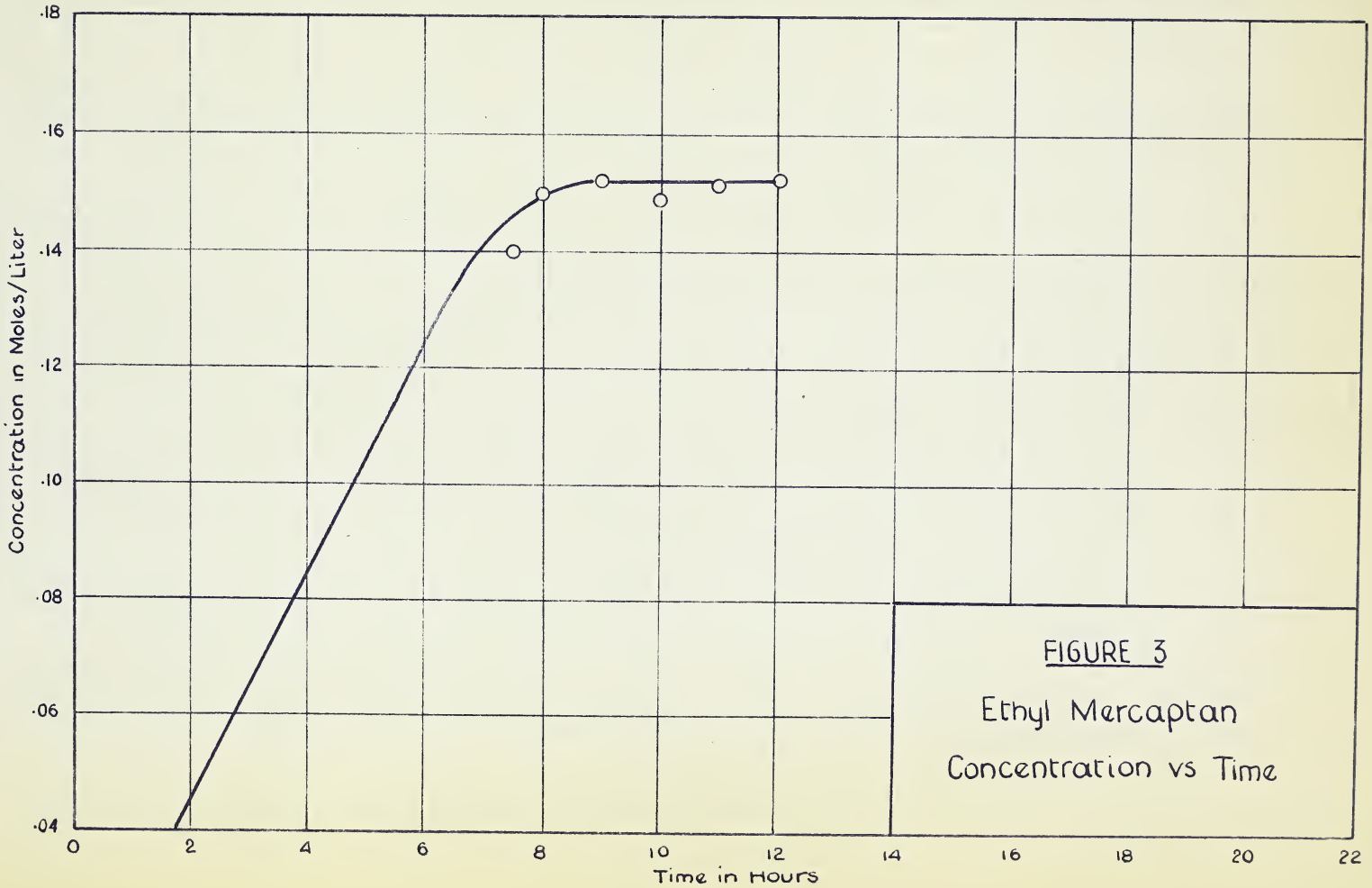

FIGURE 3

Ethyl Mercaptan

Concentration vs Time

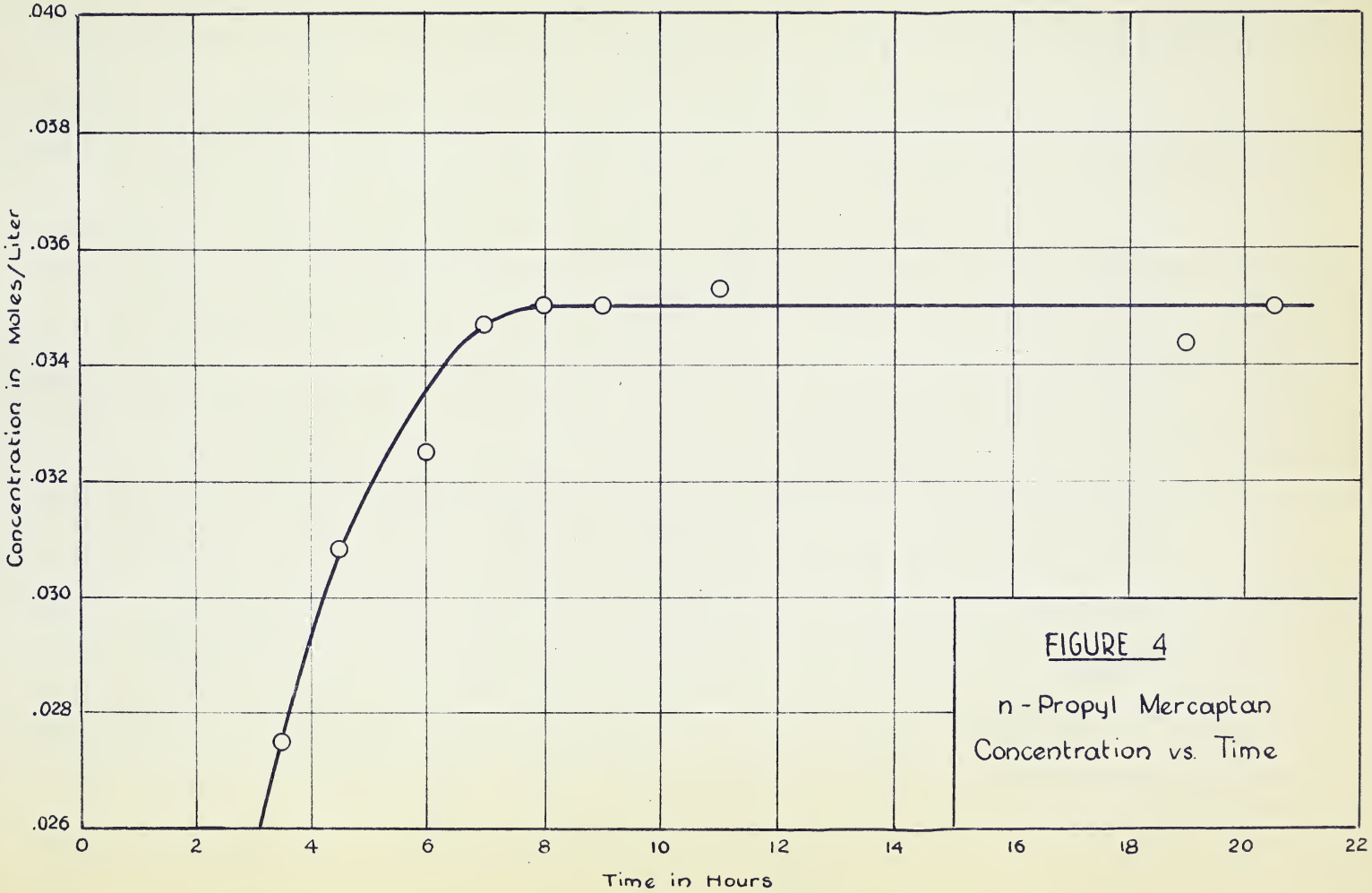

FIGURE 4

n-Propyl Mercaptan Concentration vs. Time

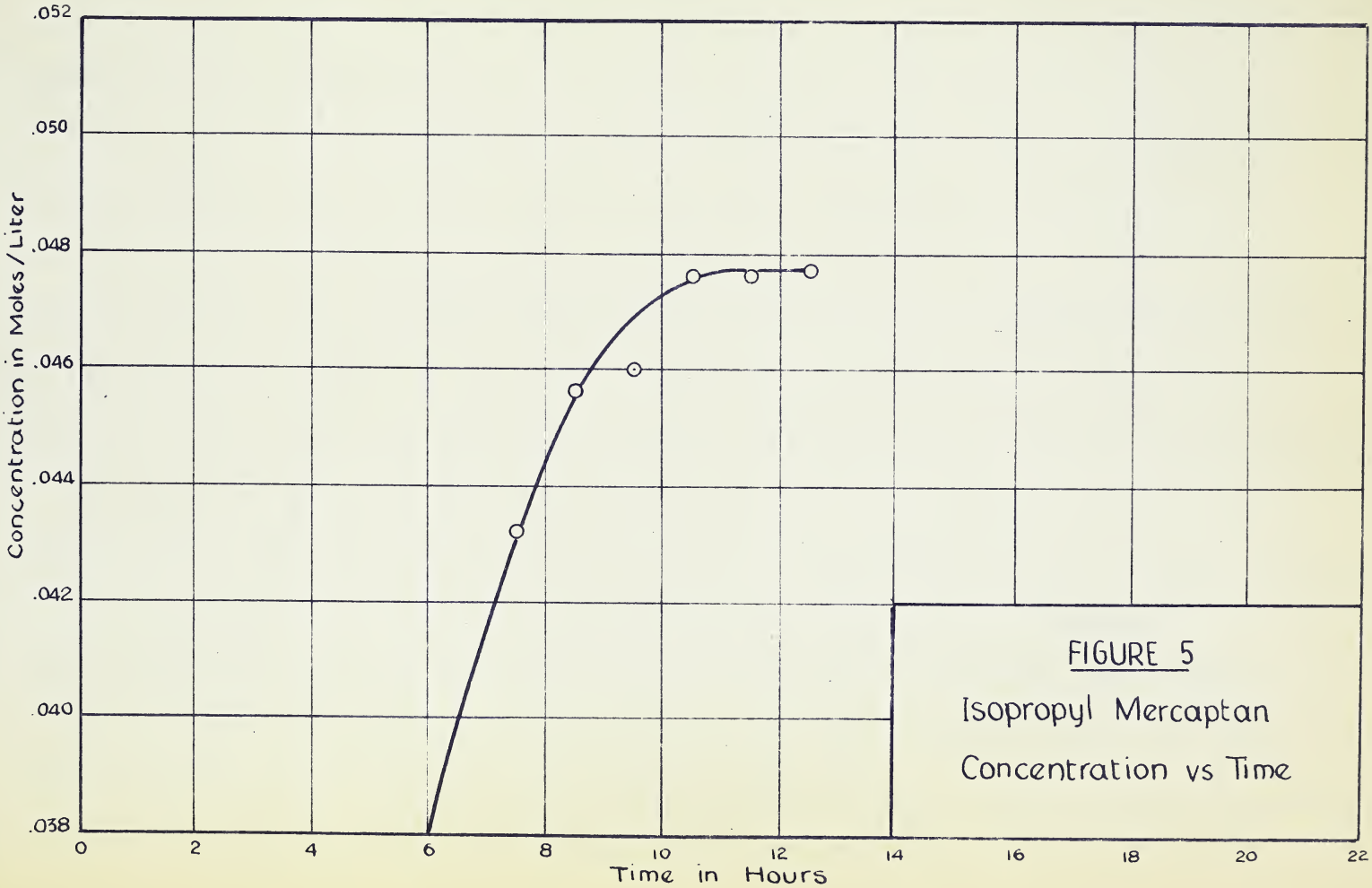

FIGURE 5

Isopropyl Mercaptan

Concentration vs Time

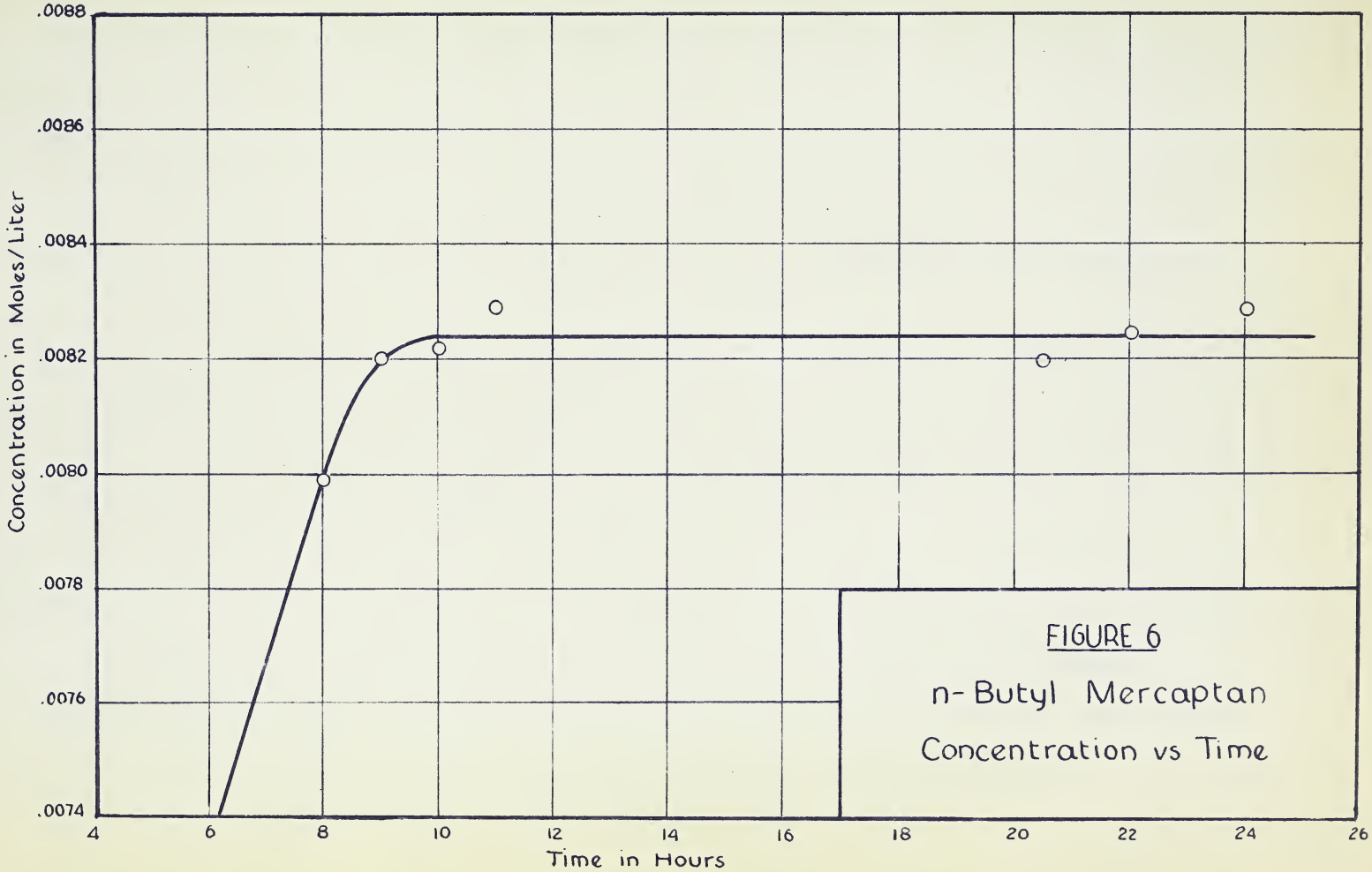

FIGURE 6

n-Butyl Mercaptan

Concentration vs Time

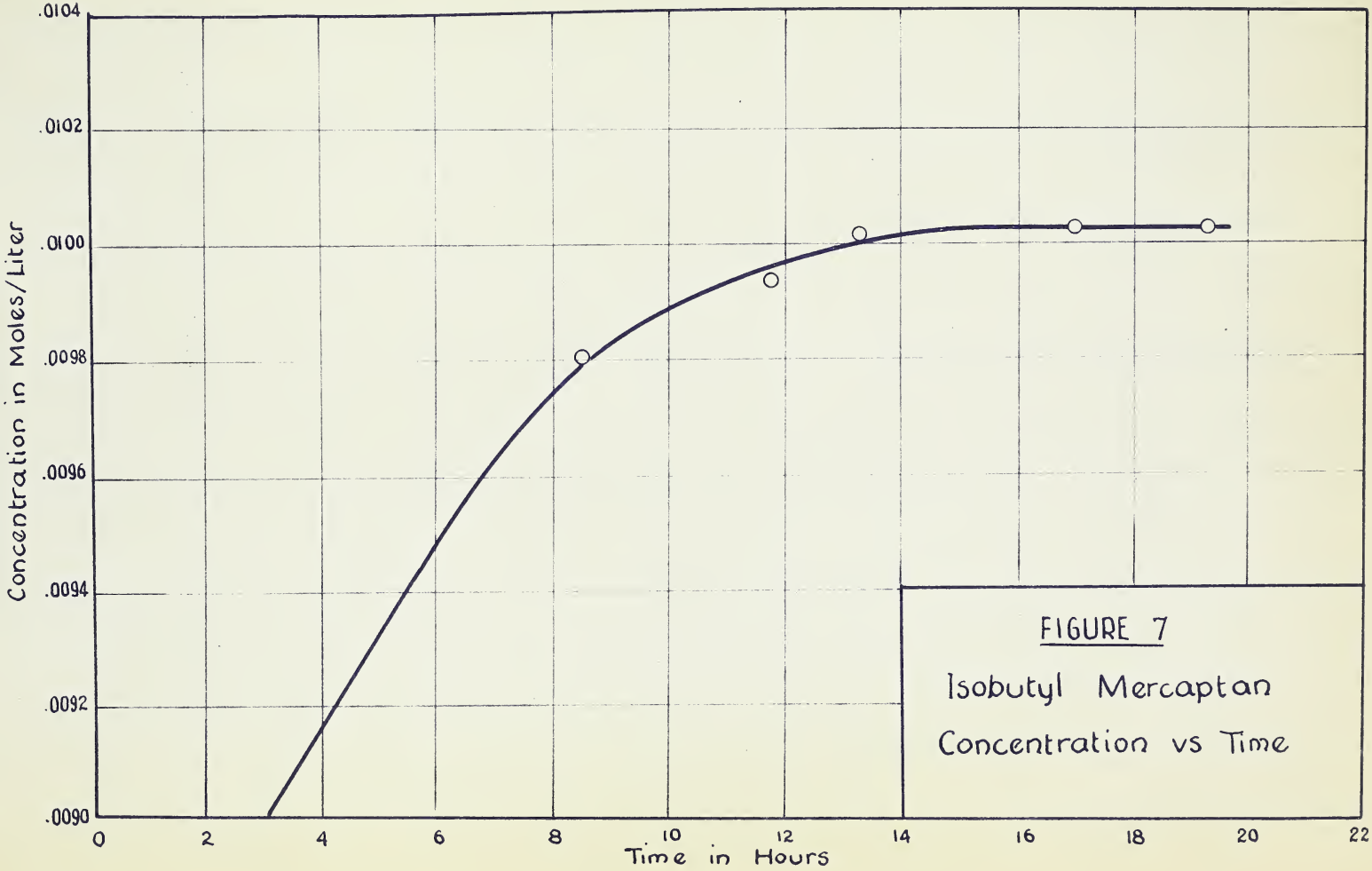

FIGURE 7

Isobutyl Mercaptan Concentration vs Time

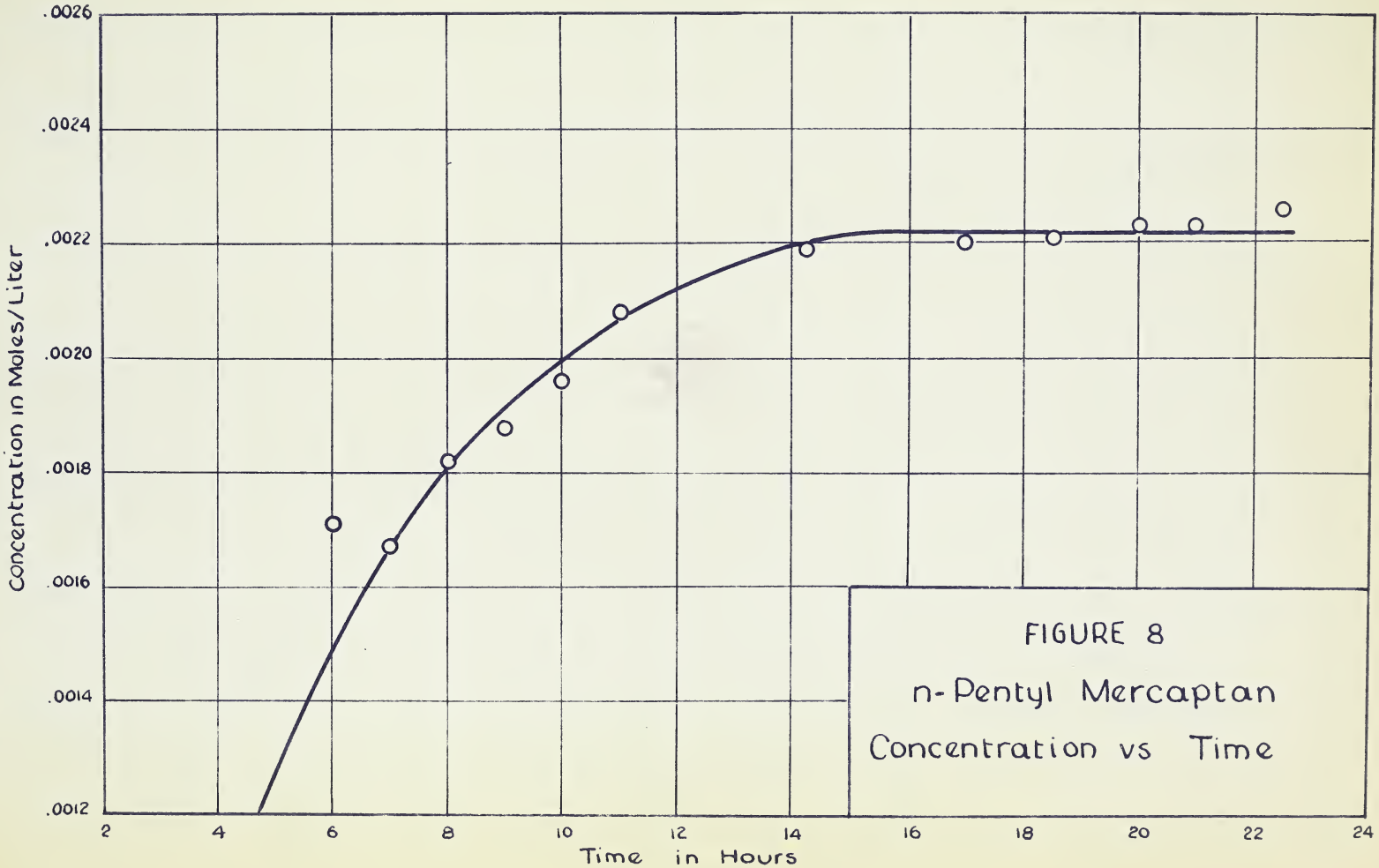

FIGURE 8

n-Pentyl Mercaptan

Concentration vs Time

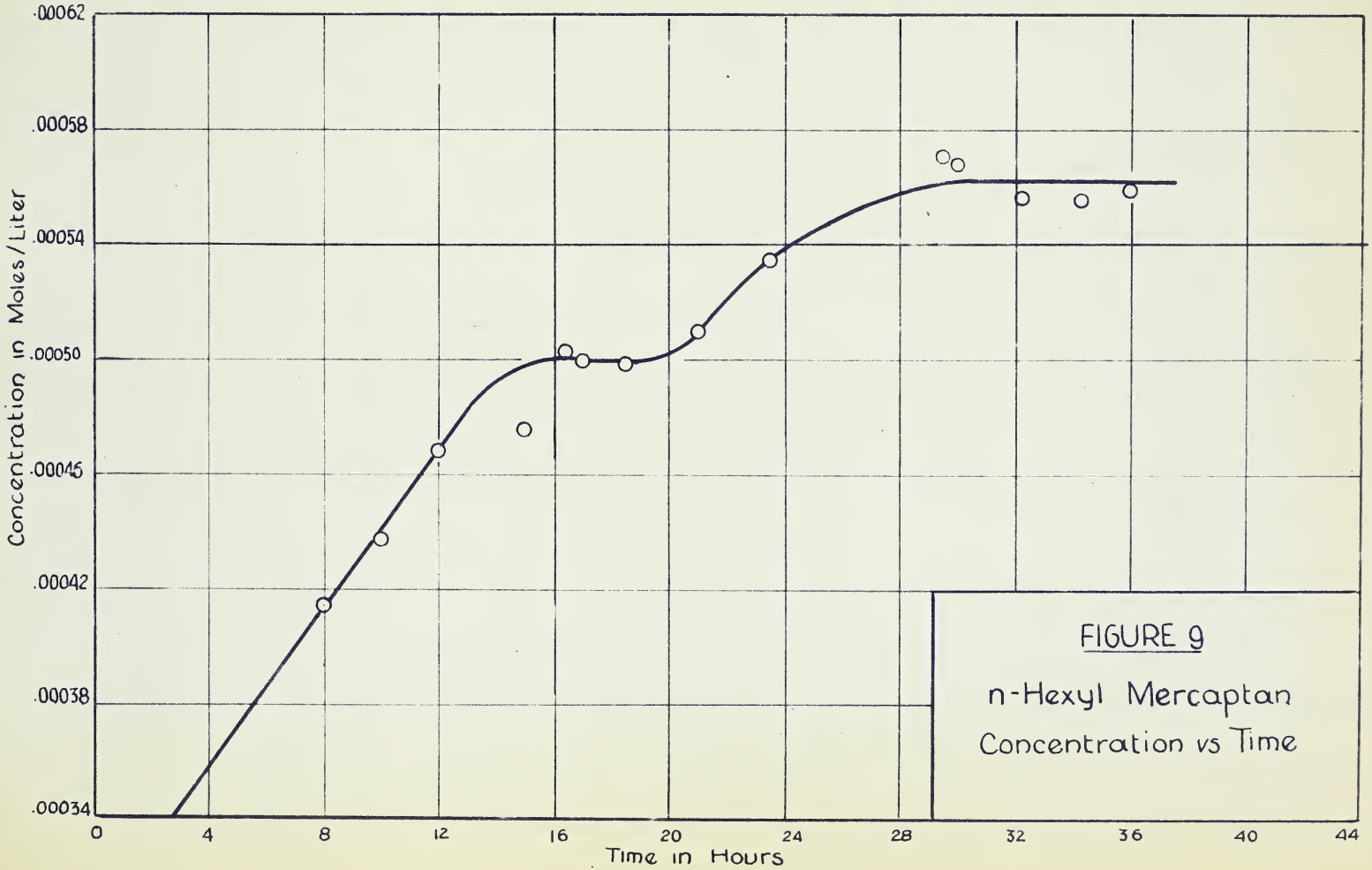

FIGURE 9

n-Hexyl Mercaptan

Concentration vs Time

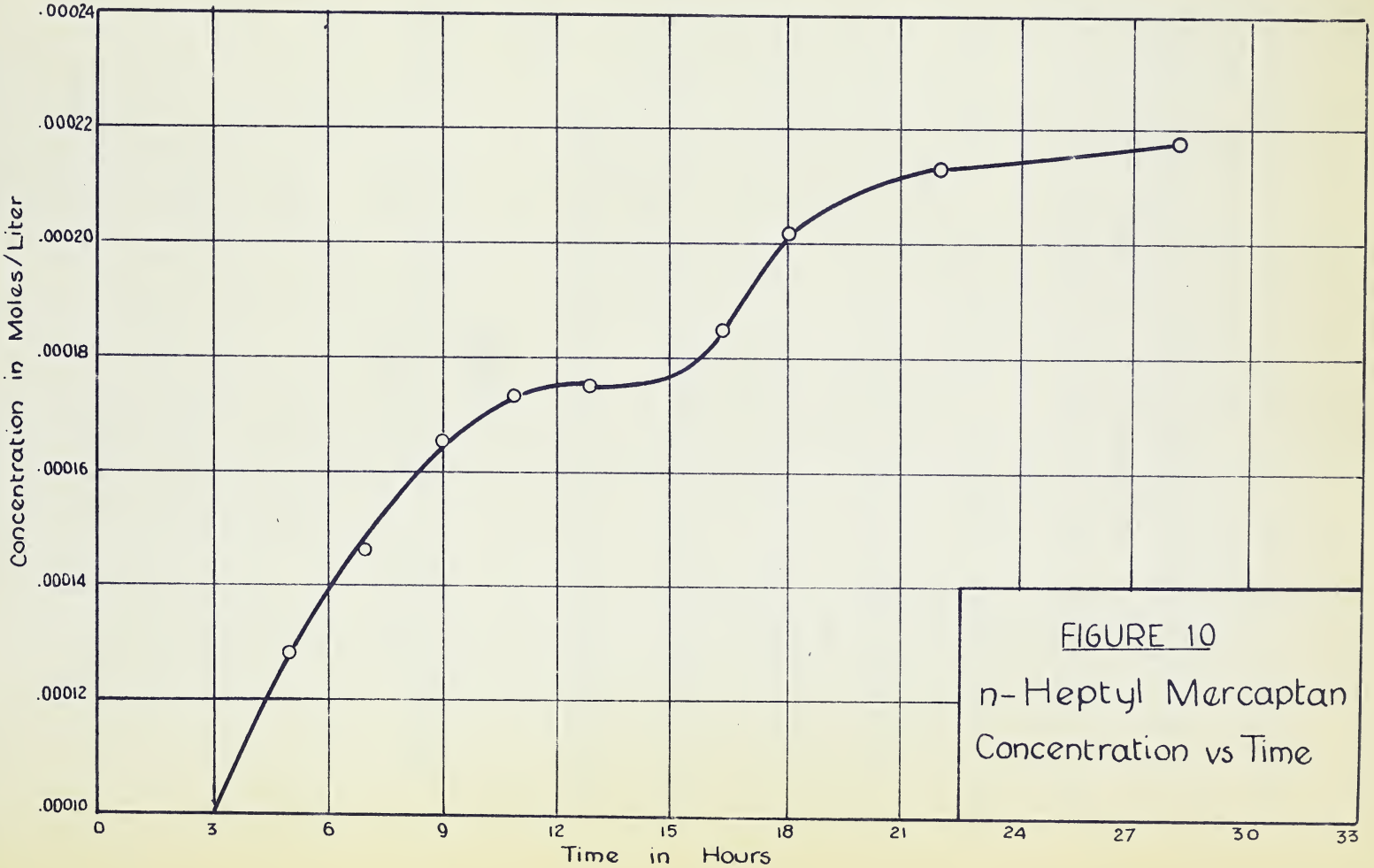

FIGURE 10

n-Heptyl Mercaptan Concentration vs Time

In about 15 hours the water solution of n - hexyl mercaptan reached a concentration which remained constant for approximately four hours. After this time the concentration increased. After about ten hours the concentration of n - heptyl mercaptan in water remained constant for four hours and then increased. No experimental work has been carried out to determine the cause of this phenomenon. One possible explanation may be the formation of disulfides in the water phase. The disulfide suspension in the water phase would extract mercaptan from the water and more mercaptan would apparently be in solution. By this means the mercaptan concentration in the water phase containing the disulfide is raised above the saturation value for pure water. The saturation concentration reported for n - hexyl and n - heptyl mercaptans is the concentration corresponding to the first plateau in the curve.

Water solubilities, which were determined, are shown in Table 6.

TABLE 6

Water Solubility of Some Low Molecular Weight Mercaptans

Mercaptan	Solubility (Moles/litre)
ethyl	1.52×10^{-1}
n - propyl	3.50×10^{-2}
isopropyl	4.77×10^{-2}
n - butyl	8.24×10^{-3}
isobutyl	10.02×10^{-3}
n - pentyl	2.22×10^{-3}
n - hexyl	5.00×10^{-4}
n - heptyl	1.75×10^{-4}

Using technical ethyl mercaptan an average solubility of 1.54×10^{-1} moles per litre was obtained at 20° and at 25°, an average value of 1.51×10^{-1} moles per litre. Although these values appear to be within the limits of experimental error, the solubility may increase slightly with a decrease in temperature. If solubility increased with decrease in temperature, it would be possible to have the burette temperature lower than 25° without danger of supersaturation of the mercaptan solution.

In most of the early experiments, it is presumed that the increasing adherence of silver mercaptide to the electrode caused a downward drift in the microammeter reading and gave low values for the current. Although the end point in these cases was at approximately the same value, the accuracy of the values is reduced due to the difficulty in taking readings, the time required to attain a steady current reading, and the small angle between the current-volume curve and the volume axis. In Figure 11 equivalent amounts of silver nitratewere titrated with mercaptan solutions and curves 1 and 2 show the current vs volume of mercaptan relationship without mercaptide interference and curve 3 shows the effect on the current of silver mercaptide coating on the rotating platinum electrode. To eliminate the adherence of silver mercaptide to the electrode, asbestos fibre was added to the solution being titrated. This was not necessary for ethyl and n-propyl mercaptans possibly due to the more crystalline nature of these precipitates.

Yabroff (13) found that plotting the common logarithm of saturation concentration against number of

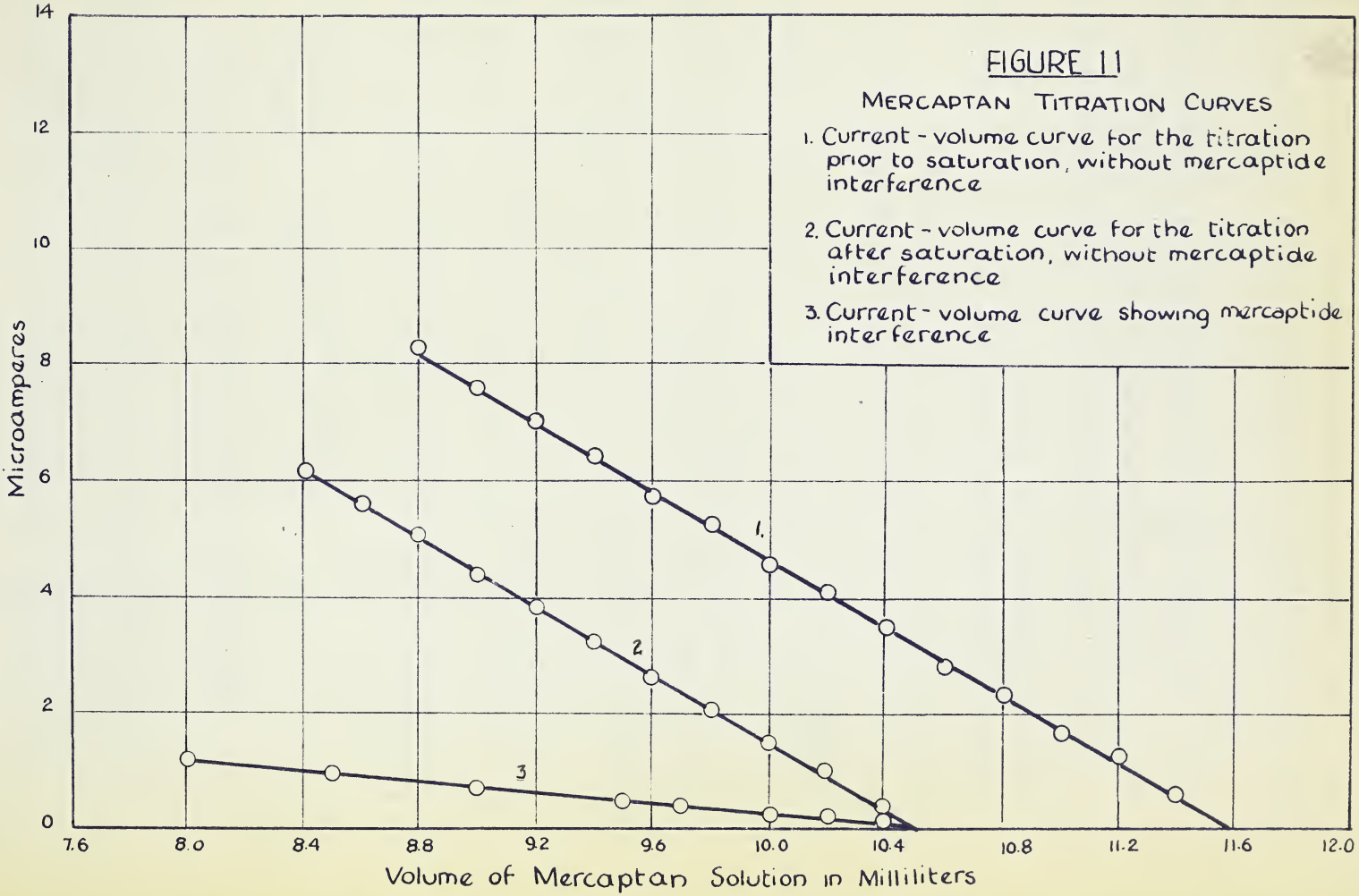
FIGURE 11
MERCAPTAN TITRATION CURVES
1. Current - volume curve for the titration prior to saturation, without mercaptide interference
2. Current - volume curve for the titration after saturation, without mercaptide interference
3. Current - volume curve showing mercaptide interference
Microamperes
0
2
4
6
8
10
12
14
7.6
8.0
8.4
8.8
9.2
9.6
10.0
10.4
10.8
11.2
11.6
12.0
Volume of Mercaptan Solution in Milliliters
1.
2
3

carbon atoms gave a straight line. Analysis, by this method, of the saturation concentrations determined in this work also gave a straight line for the mercaptans containing from two to six carbon atoms. The value for n - heptyl mercaptan was higher than expected. (see Figure 12) This could be caused by small amounts of low molecular weight mercaptan impurities. Some breakdown of the n - heptyl mercaptan may have occurred during the decomposition and distillation processes because of the high boiling point (169°) of the mercaptan. The sulfur in the mercaptan group has a greater attraction for electrons than carbon has, and may have a slight tendency to weaken the carbon-carbon bond adjacent to the sulfur. Therefore, although ordinary hydrocarbons do not undergo any appreciable amount of thermal cracking up to temperatures of 400 - 500°, it might be possible to get a small amount of cracking of n - heptyl mercaptan at the temperature of its boiling point.

The graph (Figure 12) which shows the relationship between the common logarithm of the concentration and number of carbon atoms in the mercaptan could be used to predict saturation concentrations for other mercaptans. The equation of the straight line is:

$$\log_{10} C = -0.62n + 0.38 \qquad (1)$$

where C is the saturation concentration of the mercaptan containing n carbon atoms.

Using the equation the saturation concentration would be predicted as 2.4 moles per litre for hydrogen sulfide, which corresponds to n = 0, and 0.58 moles per litre for methyl

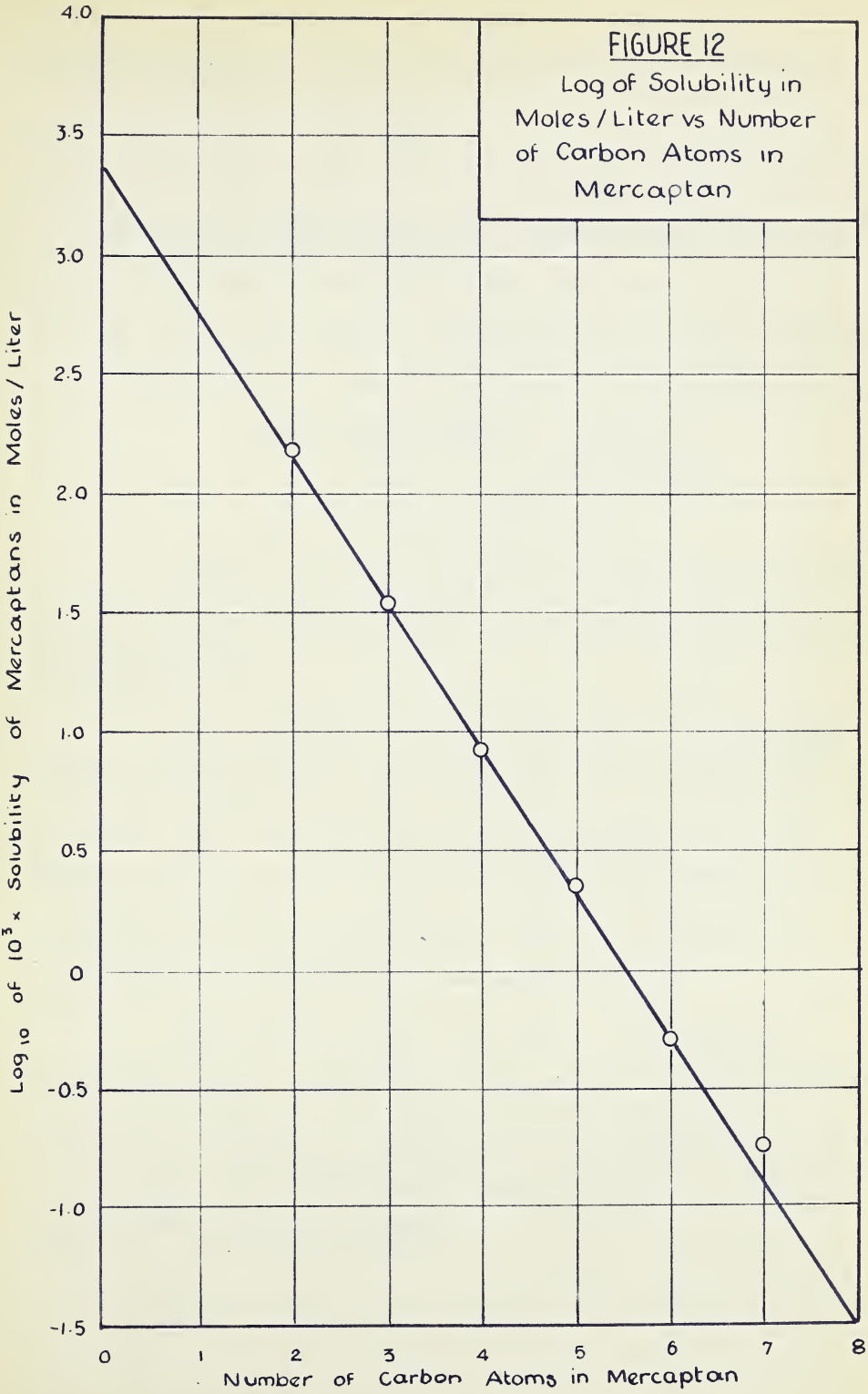
FIGURE 12
Log of Solubility in Moles / Liter vs Number of Carbon Atoms in Mercaptan
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
Log 10 of 10³ × Solubility of Mercaptans in Moles / Liter
0
1
2
3
4
5
6
7
8
Number of Carbon Atoms in Mercaptan

mercaptan. The saturation concentration of liquid hydrogen sulfide at 25° was calculated from its vapor pressure at 25° using Henry's Law in the following proportionality:

$$\frac{C_1}{C_2} = \frac{P_1}{P_2}$$

where C_1 is the saturation concentration of hydrogen sulfide gas at one atmosphere pressure, P_1.

C_2 is the saturation concentration at 25° of hydrogen sulfide at the vapor pressure of liquid hydrogen sulfide.

$$\frac{0.699 \text{ moles/litre}}{C_2} = \frac{1 \text{ atmos.}}{20.2 \text{ atmos.}}$$

$$C_2 = 2.0 \text{ moles per litre.}$$

Values used in the above calculation were interpolated from the values given in the Handbook of Chemistry and Physics (3).

The agreement between the values for hydrogen sulfide concentration, 2.0 moles per litre calculated, and 2.4 moles per litre obtained from the graph, is good. Henry's Law is most accurate at high temperatures and low pressures, and the calculations were for a system of moderately low temperature and high pressure.

Saturation values for some of the higher molecular weight mercaptans, which could be predicted from equation (1) are: n - octyl 2.7×10^{-5} moles per litre, n - dodecyl 8.8×10^{-8} moles per litre and n - hexadecyl 2.9×10^{-10} moles per litre.

CONCLUSIONS

Lead mercaptides were purified by recrystallization from appropriate solvents. The purified salt was more stable than the crude product and in most cases melted over a small temperature range. Ethyl, n - propyl, n - butyl and isobutyl mercaptides were recrystallized from an ethanol-pyridine mixture. Isopropyl mercaptide was recrystallized from ethanol. All the other mercaptides prepared were insoluble in hot ethanol. Those mercaptides which recrystallized from ethanol or ethanol - pyridine mixture would not recrystallize from benzene. n - Pentyl, n - hexyl and n - heptyl mercaptides were recrystallized from a mixture of benzene and ethanol. These mercaptides were insoluble in an ethanol - pyridine mixture.

Pure mercaptan was obtained by decomposing the lead mercaptides with dilute sulfuric acid and distilling the mercaptan. The distillate was washed with sodium carbonate solution and water, dried with anhydrous sodium sulfate and redistilled. Values for solubility using the purified mercaptans were higher than those previously reported by Yabroff and Maerov. This indicates that with low molecular weight mercaptans, the precautions taken in this study to prevent volatilization losses were important. Plotting the common logarithm of the saturation concentration of the mercaptans against the number of carbon atoms in the mercaptan produced a straight line whose equation is:

$$\text{Log}_{10} C = -0.62n + 0.38$$

where C is the saturation concentration of the mercaptan containing n carbon atoms.

Using the graph to analyze results the value for saturation concentration for n - heptyl mercaptan was higher than expected. With the higher molecular weight mercaptans, therefore, the chief problem appears to be removal of lower molecular weight mercaptan impurities.

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